PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : H01L 21/316 — A1

(11) International Publication Number: **WO 00/55895**

(43) International Publication Date: 21 September 2000 (21.09.00)

(21) International Application Number: PCT/KR00/00204

(22) International Filing Date: 14 March 2000 (14.03.00)

(30) Priority Data:
1999/8740 16 March 1999 (16.03.99) KR

(71) Applicant *(for all designated States except US)*: GENITECH, INC. [KR/KR]; 1694–5, Sinil–dong, Taedok–ku, Taejon 306–230 (KR).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: KOH, Won–Yong [KR/KR]; 105–605 Hanul Apt., 160–1, Shinsung–dong, Yusong–gu, Taejon 305–345 (KR).

(74) Agent: HUH, Jin–Seok; J.S. Huh Patent Office, 206 Sungji Building, 1338–22, Seocho–dong, Seocho–ku, Seoul 137–070 (KR).

(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
In English translation (filed in Korean).

(54) Title: METHOD OF FORMING AN ALUMINUM OXIDE FILM

(57) Abstract

The present invention relates to a method of forming an aluminum oxide film for use in semiconductor devices on a substrate. Organo–aluminum compound and alcohol, which are sources for the aluminum oxide film formation, are first prepared as gas phases, respectively. Then the gas phase sources are sequentially applied to the substrate to form an aluminum oxide film. In general, alcohol can be evacuated faster than water vapor in a vacuum chamber, which significantly reduces time required for source supply cycle. Therefore, according to the present invention, the growth rate of the aluminum oxide filmn can be increased compared with prior art methods. In addition, the cost associated with semiconductor device fabrication can be reduced because the temperature of both gas supply unit and a reactor can be decreased.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

METHOD OF FORMING AN ALUMINUM OXIDE FILM

TECHNICAL FIELD

The present invention relates to a method of forming an aluminum oxide film, and more particularly to a method of forming an aluminum oxide film on a substrate for semiconductor devices.

BACKGROUND ART

Aluminum oxide film is well known to be used widely not only for optical purposes but also for protection films, gate oxide films and optical lithography masks for semiconductor devices as shown in the reference 1. (reference 1: E. Fredriksson and J.O. Carlsson, *Journal of Chemical Vapor Deposition*, vol. 1, p. 333 (1993)) Furthermore, reference 2 reported the use of aluminum oxide film for protection from hydrogen diffusion by forming an ultra-thin aluminum oxide film on a PZT($PbZrTiO_3$) dielectric layer of a FeRAM(Ferroelectric Random Access Memory) (reference 2: Sang Min Lee, Young Kwan Park, In Son Park, Chang Soo Park, Cha Young Ryu, Sang In Lee, Mun Yong Lee, *Abstract of the 5th Korean Semiconductor Society* p. 255 (1998)).

Compared to the conventional chemical vapor deposition method which provides source materials of a thin film simultaneously, the sequential supply of source materials on a substrate can form a thin film only by a chemical reaction on a substrate surface. Therefore, the latter method can grow a thin film of uniform thickness irrespective of uneven substrate surface, and can control precisely film thickness because the growth of film depends not on process time but on the number of source material supply cycles. It is well described in the "Atomic Layer Epitaxy" edited by T. Suntola and M. Simpson (reference 3: T. Suntola and M. Simpson eds. *Atomic Layer Epitaxy*, Blackie, London (1990)).

As an application of the latter method, the formation of aluminum oxide film having a uniform thickness on an uneven substrate surface by a sequential supply of trimethylaluminum and water vapor was proposed in the reference 4. (reference 4: Y. Kim, S. M. Lee, C. S. Park, S. I. Lee, and M. Y. Lee, *Applied Physics Letters*, vol. 71, p. 3604 (1997)). Referring to the reference 4, trimethylaluminum, argon, water vapor

and argon are sequentially supplied for 1, 14, 1, and 14 seconds, respectively in each cycle while keeping the substrate at a temperature of 370°C in a reactor heated at 150°C. In each source material supply cycle, the film grows by 0.19nm which makes the total film growth rate of 0.38nm/min. This growth rate is too slow to be applied to semiconductor device fabrication. In order to enhance the film growth rate, each source material supply cycle should be shortened. In the technology disclosed in the reference 4, water vapor is used in the film growth. However, the water vapor is difficult to evacuate in a vacuum chamber, which makes the decrease of material supply cycle time difficult.

Furthermore, in case of using water vapor for the formation of an aluminum oxide film, the reactor and the gas supply unit where the water vapor passes should be kept at high temperature because water vapor is easily condensed in a cold unit. It increases energy consumption and workers may get burned during the operation and maintenance of the equipment.

DISCLOSURE OF INVENTION

Accordingly, it is an object of the present invention to provide a method of forming an aluminum oxide film by employing source materials which can be easily evacuated in a vacuum chamber and are less susceptible to condense in a reactor.

It is another object of the present invention is to provide a method which can form an aluminum oxide film faster than the method which employs water vapor.

In order to achieve the above objects, the method of forming an aluminum oxide film of the present invention comprises the steps of: preparing gases of organo-aluminum compound and alcohol for forming an aluminum oxide film; and contacting said gases sequentially and repeatedly onto a substrate.

The number of carbons in the alcohol molecule is preferably from 2 to 6, and more preferably the alcohol is isopropanol which is widely used in the semiconductor device fabrication.

Furthermore, the organo-aluminum compound is preferably trialkylaluminum, and more preferably the trialkylaluminum is trimethylaluminum.

BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiment of the present invention will be described below.

First of all, trimethylaluminum and isopropanol are gasified and are supplied into a deposition chamber. Argon gas is provided as a purge gas between the supplies of the gasified trimethylaluminum and isopropanol. Because isopropanol has a high vapor pressure, it is supplied into the reactor directly using a carrier gas without an additional heating process. Trimethylaluminum gas, argon purge gas, isopropanol gas and argon purge gas are sequentially supplied for 2, 2, 2 and 2 seconds, respectively in each cycle which makes the gas supply period of 8 seconds. The trimethylaluminum decomposes above 300°C, so the source materials must be supplied at a temperature lower than 300°C to grow a film only by a surface reaction. When the film is grown on a substrate kept at 250 ~ 290 °C, the film growth rate by measuring the film thickness using an ellipsometer is determined to be 0.08nm per source material supply cycle or 0.60nm/min.

INDUSTRIAL APPLICABILITY

According to this invention, the temperature for gas supply unit and a reactor can be lowered compared to the previous methods. It can, therefore, simplify apparatus necessary for fabricating semiconductor devices and lower manufacturing cost. Furthermore, an aluminum oxide film with superior step coverage can be grown faster than prior art methods.

WHAT IS CLAIMED IS :

1. A method of forming an aluminum oxide film comprising the steps of:

preparing gases of organo-aluminum compound and alcohol for forming an aluminum oxide film; and

contacting said gases sequentially and repeatedly onto a substrate.

2. The method according to claim 1, wherein the number of carbons in said alcohol molecule is from 2 to 6.

3. The method according to claim 2, wherein said alcohol is isopropanol.

4. The method according to any of claims 1 to 3, wherein said orgoano-aluminum compound is trialkylaluminum.

5. The method according to claim 4, wherein said trialkylaluminum is trimethylaluminum.

6. The method according to claim 1, wherein the temperature of substrate is kept at 250 ~ 290°C at the step of contacting said gases sequentially and repeatedly onto a substrate.

INTERNATIONAL SEARCH REPORT

international application No.
PCT/KR00/00204

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 H01L 21/316

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimun documentation searched (classification system followed by classification symbols)

IPC7 H01L 21/316

Documentation searched other than minimun documentation to the extent that such documents are included in the fileds searched

Korean Patents and applicatins for inventions since 1975
Korean Utility models and applicatins for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search trerms used)

KIPONET

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
D, A	Applied Physics Letters, Vol 71, Page 3604, 1997	1, 5

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevence

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevence; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 JUNE 2000 (26.06.2000)	29 JUNE 2000 (29.06.2000)

Name and mailing address of the ISA/KR	Authorized officer
Korean Industrial Property Office Government Complex-Taejon, Dunsan-dong, So-ku, Taejon Metropolitan City 302-701, Republic of Korea	SHIN, Chang Woo
Facsimile No. 82-42-472-7140	Telephone No. 82-42-481-5733